Some Properties of the Calcium Aluminoferrite Hydrates

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards

Announcing—The Building Science Series

The "Building Science Series" disseminates technical information developed at the Bureau on building materials, components, systems, and whole structures. The series presents research results, test methods, and performance criteria related to the structural and environmental functions and the durability and safety characteristics of building elements and systems.

These publications, similar in style and content to the NBS Building Materials and Structures Reports (1938–59), are directed toward the manufacturing, design, and construction segments of the building industry, standards organizations, officials responsible for building codes, and scientists and engineers concerned with the properties of building materials.

The material for this series originates principally in the Building Research Division of the NBS Institute for Applied Technology. Published or in preparation are:

BSS1. Building Research at the National Bureau of Standards. (In preparation.)

* BSS2. Interrelations Between Cement and Concrete Properties, Part 1. Materials, Techniques, Water Requirements, and Trace Elements. 35 cents.

* BSS3. Doors as Barriers to Fire and Smoke. 15 cents.

* BSS4. Weather Resistance of Porcelain Enamels: Effect of Exposure Site and Other Variables After Seven Years. 20 cents.

* BSS5. Interrelations Between Cement and Concrete Properties, Part 2. Sulfate Expansion, Heat of Hydration and Autoclave Expansion. In press.

RELATED PUBLICATIONS

* NBS Monograph 28—Causes of Variation in Chemical Analyses and Physical Tests of Portland Cement—25 cents

---

* NBS Monograph 43—Chemistry of Cement
  Proceedings of the Fourth International Symposium—Washington 1960. Presented in two volumes. Volume I—$6.50. Volume II—$6.25. The two volumes at $12.75 a set. (Originally issued September 1962, and reprinted February 1964).

Some Properties of the Calcium Aluminoferrite Hydrates

Elmer T. Carlson

Building Research Division
Institute for Applied Technology
National Bureau of Standards
Washington, D. C.

Contents

Some Properties of the Calcium Aluminoferrite Hydrates

Elmer T. Carlson

Calcium aluminoferrite hydrates in two series, $4CaO \cdot (Al_2O_3, Fe_2O_3) \cdot n\ H_2O$ (hexagonal plates) and $3CaO \cdot (Al_2O_3, Fe_2O_3) \cdot 6\ H_2O$ (isometric), were prepared from the anhydrous aluminoferrites by hydration in the presence of $Ca(OH)_2$. The hexagonal phase was stable below 15 °C, the isometric above 35 °C, in contact with solution. The end member, $2\ CaO \cdot Fe_2O_3$, did not produce an isometric hydrate, however. X-ray diffraction patterns of the hexagonal series in the 19 H_2O stage of hydration were indistinguishable from patterns of $4\ CaO \cdot Al_2O_3 \cdot 19\ H_2O$. After drying to the 13-hydrate stage, slight differences in the patterns were observed. The isometric series shows a definite shift in x-ray pattern with change in Fe_2O_3/Al_2O_3 ratio, the unit-cell edge increasing from 12.573 for $3\ CaO \cdot Al_2O_3 \cdot 6\ H_2O$ to 12.716 for the member having Fe_2O_3/Al_2O_3 close to 5. DTA traces show endotherms near 100 and 200 °C corresponding to dehydration stages of the hexagonal series and one near 300 °C representing the first dehydration stage of the isometric phase. The hexagonal hydrates are converted to the isometric during the course of the DTA run. The peak attributed to the isometric phase shifts from 323 to 290 °C going from the pure aluminate to the member richest in Fe_2O_3. All the aluminoferrite hydrates, both hexagonal and isometric, reacted with $CaSO_4$ solution to give products of the monosulfate and trisulfate (ettringite) types, the latter predominating at later stages. The rate of reaction decreased with increasing Fe_2O_3 content.

Key Words: Calcium aluminoferrite hydrates; calcium sulfate reaction with calcium aluminoferrite hydrates; DTA of calcium aluminoferrite hydrates; x-ray patterns of calcium aluminoferrite hydrates.

1. Introduction

In the manufacture of portland cement clinker of normal composition, the iron which is always present in the raw materials enters into a ternary composition with calcium oxide and alumina to form a reddish-brown crystalline calcium aluminoferrite. Although this phase is commonly referred to simply as tetracalcium aluminoferrite, $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ (frequently abbreviated to C_4AF[1]) the composition is known to be variable. The existence of a solid-solution series between the known C_2F and a hypothetical C_2A, extending as far as C_6A_2F, has been shown by previous investigators [1][2]. However, the range of composition to be expected in cement clinker is considerably narrower. A review of research in this field up to 1964 has been given by Welch [2]. In a more recent paper, Majumdar [3] places the limit at 70 mole-percent C_2A.

The calcium aluminoferrite phase resembles the other major constituents of cement clinker in that it reacts with water to form crystalline hydrated compounds and thereby sets to a hard polycrystalline mass. In a previous paper [4] it was shown that the rate of solution and hydration is a function of the composition (ratio of Fe_2O_3 to Al_2O_3, or F/A) and that the composition of the hydrated phases also varies with that of the anhydrous material.

In the present study the composition and properties of the hydration products are explored in greater detail.

Research on the preparation of the hydrated calcium ferrites and aluminoferrites has, in general, followed the same lines that have been found satisfactory for preparation of the hydrated calcium aluminates. The most important difference is that the method based on precipitation from clear supersaturated solutions, which is of great utility in making the aluminates, is less satisfactory for the aluminoferrites and cannot be used at all for the ferrites because of their low solubility. It has been shown [1,5,6,7] that there is a hydrated tetracalcium ferrite, crystallizing in hexagonal plates, probably isostructural with tetracalcium aluminate hydrate; also that there is a solid solution series between the two. There is also a hydrogarnet solid solution series extending from C_3AH_6 almost to C_3FH_6, but in this case the existence of the ferrite end member is in doubt. It has not been established that there are iron-bearing analogs of the known aluminates C_2AH_8 and CAH_{10}. No evidence of such compounds was observed in the present investigation.

The purpose of this study is twofold: (1) to relate certain identifying characteristics of the hydrated compounds to their composition, and (2) to ascertain the effect of composition on certain properties of the materials which may be of significance because of their effect on the behavior of cement.

---

[1] The abbreviated formulas frequently adopted by cement chemists will be used in this paper when there is no danger of ambiguity, C = CaO; A = Al_2O_3; F = Fe_2O_3; H = H_2O.

[2] Figures in brackets indicate the literature references at the end of this paper.

2. Materials and Procedures

The calcium aluminoferrite hydrates were prepared by reaction of a series of powdered anhydrous calcium aluminoferrites with water and calcium hydroxide. Pertinent composition data for the anhydrous materials are given in table 1. Additional data and details of preparation have been

TABLE 1. *Chemical composition of anhydrous aluminoferrite preparations*

Designation	CaO	Al₂O₃	Fe₂O₃	Molar ratio $\dfrac{Fe_2O_3}{Al_2O_3 + Fe_2O_3}$
	%	%	%	
Fss–1	48.2	28.8	23.3	0.341
Fss–2	47.1	24.4	28.5	.427
Fss–3	46.3	21.0	32.8	.500
Fss–4	45.2	17.3	37.5	.580
Fss–5	44.3	13.5	42.1	.666
Fss–6	42.6	6.4	51.0	.837
C₂F–1	41.1	0.0	59.0	1.000

reported previously [4]. In most cases, CaO or $Ca(OH)_2$ was added either in excess or in the amount required by the stoichiometry of the reaction. As reported previously [4], hydration in the absence of added lime is accompanied by hydrolysis, and the hydrates are more basic than the anhydrous materials, It was also observed that the crystalline products generally contained less iron than did the anhydrous materials and that the rest of the iron separated as an apparently amorphous form of Fe_2O_3. It was anticipated that hydration in the presence of lime would result in crystalline products having the same ratio of iron to aluminum as present in the anhydrous materials. Results compatible with this expectation recently have been reported by Schwiete and Iwai [7].

The hydration was accomplished in several ways, none of which was entirely satisfactory in all respects. The experiments were not conducted in a glove box; however, contamination with atmospheric carbon dioxide was minimized by such precautions as sweeping out containers before use with air previously passed through a CO_2-absorbent, filtration in a closed system, and rapid handling when containers were opened for any reason. The x-ray patterns afforded a check on the extent of exclusion of CO_2, since the strong (001) line of β-tetracalcium aluminate hydrate could be distinguished from that of the α-hydrate (currently believed to contain CO_2) and from the corresponding line of the monocarbonate. In many cases there was no evidence of either of the latter compounds; nevertheless, it must be assumed that a slight amount of carbonation did occur in every experiment.

The first method consisted of adding a weighed amount of the anhydrous powder (about 2 g), plus enough $Ca(OH)_2$ to convert it all to tetracalcium aluminoferrite hydrate, $C_4(A,F)H_n$, to 100 ml of saturated $Ca(OH)_2$ solution in a polyethylene bottle, and storing at 1 °C with occasional shaking. The low temperature was chosen to insure formation of the hydrates of the hexagonal type. The reaction rate varied with the composition, becoming slower as the Fe_2O_3 content increased. The sample highest in Al_2O_3 was completely converted to hydrate in a few months, except for a few consolidated lumps of anhydrous material. Samples high in Fe_2O_3 were not completely hydrated after one year. The reaction products were white and very finely divided. A sample of C_3A was put through the same procedure. This method will be referred to in the following as method A.

The next method used was similar except that the reaction was accelerated by working at room temperature, by frequent or continuous shaking, and by adding a charge of plastic beads or small steel balls. Storage at 45 °C was another variation tried. These modifications, which will be referred to collectively hereafter as method B, proved relatively unsuccessful, especially with the starting materials high in Fe_2O_3. The steel balls were very effective in speeding up the reaction, but the products quickly became contaminated with extremely minute particles of metallic iron resulting from abrasion. The plastic beads were relatively ineffective. Storage at 45 °C soon resulted in hydrolysis and liberation of Fe_2O_3, except for the three members of the series lowest in this component. Despite these limitations, a few products satisfactory for further study were obtained by this general method.

Method C, which was in many respects the most satisfactory of those used, consisted of grinding the sample, mixed with a slight excess of $Ca(OH)_2$ and about 25 ml of water, with a motor-driven mortar and pestle. To exclude CO_2, a close fitting tent of sheet plastic was placed over the apparatus and a stream of air previously bubbled through a lime suspension was introduced directly above the mortar. The operation was started at room temperature, but the heat developed by the motor resulted in a rise to as high as 40 °C during the grinding. Hydration of the materials highest in alumina was practically complete in 2 hours, while the C_2F was still incompletely hydrated after 7 hours. It must be assumed that some solid material was abraded from the mortar and pestle. However, only approximately 0.1 percent of silica was found gravimetrically in two of the hydrated products selected for analysis.

The hydrated products were filtered through fritted glass crucibles and dried over saturated NH_4Cl solution (approximately 79% rh) in a partially evacuated desiccator.

X-ray diffraction patterns of the powdered preparations were made on a diffractometer using filtered copper K_α radiation. Patterns of the platy-crystalline materials show strong orientation effects, since no special precautions were taken to avoid packing when mounting specimens. The

hydrogarnets, forming equidimensional grains, present no problem in this respect.

The apparatus used for differential thermal analysis (DTA) consisted of a cylindrical block of aluminum about 4.5 cm in diameter and 5.5 cm in height, heated by a small cartridge heater located axially. Two wells were provided for the sa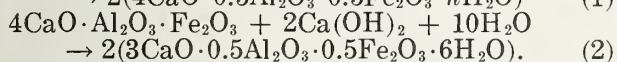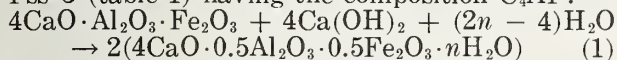mple and the reference couple, respectively. The sample, weighing about 50 mg, was placed in a glass tube which was then placed in the block and the thermocouple junction was set just below the surface of the sample. The upper operating limit was about 400 °C. The heating rate varied somewhat, starting at about 15 °C/min and decreasing to about 10 °C/min at the end of the run.

3. Experimental Results and Discussion

3.1. General Observations

A study of the relation between the composition of the hydrates and their properties requires a knowledge of the composition. This cannot be determined directly unless it is known that only a single phase is present in the reaction product, hence it is necessary to rely on indirect evidence. We may consider a pair of idealized reactions, selecting for example the anhydrous preparation Fss–3 (table 1) having the composition C_4AF:

$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 4Ca(OH)_2 + (2n - 4)H_2O$$
$$\rightarrow 2(4CaO \cdot 0.5Al_2O_3 \cdot 0.5Fe_2O_3 \cdot nH_2O) \qquad (1)$$
$$4CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 2Ca(OH)_2 + 10H_2O$$
$$\rightarrow 2(3CaO \cdot 0.5Al_2O_3 \cdot 0.5Fe_2O_3 \cdot 6H_2O). \qquad (2)$$

Similar equations could be written for the other preparations, differing only in the relative amounts of Al_2O_3 and Fe_2O_3. The anhydrous compound is deep brown in color, varying in shade with the proportion of Fe_2O_3 present. The reaction products are white, or perhaps cream-colored at the high-iron end of the series. Hence the disappearance of the brown color is a fair index of completeness of the reaction.

On the basis of data in the literature [1,2,5] and the compatibility of results reported herein with such data, the ratio of CaO to $Al_2O_3 + Fe_2O_3$ in the product, namely, 4 to 1 in the first equation and 3 to 1 in the second, may be accepted as correct. The number of molecules of water is, for present purposes, of little concern. The only uncertainty is in the ratio of Al_2O_3 to Fe_2O_3 in the products. If the hydration reaction were to result in a product richer in alumina than the parent material, part of the Fe_2O_3 would have to appear in some other form. Experience has shown [4] that under similar conditions it readily separates as amorphous Fe_2O_3 (or possibly a hydrate) which is easily recognizable by its brick-red color. As noted above, this type of coloration was observed in some experiments, especially at 45 °C and with high Fe_2O_3 content. It was not observed, however, in the hydrates prepared at 1 °C. The converse possibility, that of an increase in Fe_2O_3/Al_2O_3 ratio on hydration with some liberation of Al_2O_3, would be harder to detect, since either hydrated Al_2O_3 or any possible calcium aluminates formed would be white. Inasmuch as the splitting off of part of the Fe_2O_3 was observed to occur rather readily, it was tentatively assumed that the liberation of Al_2O_3 would be unlikely to occur. As will be shown later, this assumption is not necessarily valid under all circumstances.

3.2. Effect of Temperature

The hydrates produced at 1 °C were all of the hexagonal-plate type. At room temperature the products were mixtures of the plate crystals and those of the hydrogarnet type, except in the case of C_2F which never produced any hydrogarnet type. Hydration at 45 °C gave an increased proportion of hydrogarnet (again with the exception of C_2F). As previously noted, the preparations higher in iron liberated Fe_2O_3 at this temperature. Excess CaO was present as crystals of $Ca(OH)_2$.

By changing the temperature of storage of the aqueous suspensions, it was possible to convert the hexagonal hydrates to the isometric, or vice versa. A moderately narrow range of coexistence of the two phases was found for the calcium aluminate hydrates and for the preparations low in iron. The conversion became more sluggish and less complete as the iron content increased. The microscope proved very useful for these experiments. For example, in a suspension of calcium aluminate hydrates containing both hexagonal (C_4AH_{19}) and isometric (C_3AH_6) crystals, the faces of the latter were observed to be clear and sharp. After the suspension was kept 1 day at 10 °C the crystals were altered on the surface, evidently through formation of plates of C_4AH_{19}. After 2 additional days at 30 °C the C_3AH_6 crystals again were clean. Three more days at 15 °C produced the surface alteration again, 1 day at 30 °C again removed it, after which 14 days at 20 °C caused no change. On the basis of this evidence, confirmed by x-ray diffraction analysis, the equilibrium temperature for the reaction C_4A hyd. $\leftrightarrows C_3A$ hyd. $+ CH$ is placed between 15 and 30 °C. Seligmann and Greening [8], using an ingenious x-ray technique, have demonstrated the reversibility of this reaction on varying the temperature.

Conversion temperature ranges for the Fss series, determined by the cycling procedure described above, are given in table 2. The hydrates used for these experiments were prepared by method C, except for No. 1 which was prepared by method A (see preceding section).

TABLE 2. *Approximate temperatures of reversible reaction between hexagonal hydrates and hydrogarnets in presence of saturated* $Ca(OH)_2$

No.	$\dfrac{F}{A + F}$	Crystal form of orig. prepn.	Reaction[a] hg → hex[c]	Reaction[b] hex → hg[c]
			°C	°C
1	0	hex	15	30
2	0.194	hg	15	35
3	.341	hg	18	30
4	.427	hg + hex	18	25
5	.500	hg	20	30
6	.580	hg	18	35
7	.666	hg + hex	15	35
8	.837	hg + hex	15	35
9	1.000	hex		

[a] Highest temperature at which this reaction was observed.
[b] Lowest temperature at which this reaction was observed.
[c] hg = hydrogarnet.
   hex = hexagonal plate phase.

3.3. X-ray Diffraction Patterns

a. Hexagonal Series

Portions of the first series of hydration products (prepared by prolonged storage at 1 °C) were filtered off and mounted in the x-ray diffractometer while still moist. High humidity was maintained in the chamber surrounding the mount. Under these conditions, patterns similar to that of the fully hydrated tetracalcium aluminate ($4CaO \cdot Al_2O_3 \cdot 19H_2O$ [9]) were obtained. However, the basal plane reflections were greatly magnified in relation to the intensities of the other reflections because of preferred orientation of the thin, platy crystals as mounted. As many as eight orders of the strongest reflection were recorded, while other expected lines were either weak or entirely absent. Thus it was not possible to establish a relation between the Fe_2O_3/Al_2O_3 ratio and the spacings or intensities of the weaker x-ray lines. The d-spacing for the strong (001) line appeared to shift linearly from 10.72 to 10.59 Å, going from the C_4A to the C_4F hydrate. However, this difference is so slight as to be within the error of measurement at this low angle. As a check experiment to cancel out machine errors, a composite of the C_4A hydrate preparation with the hydrated C_4AF (preparation Fss–3) was prepared by mixing equal amounts of the suspensions and filtering. The x-ray diffraction pattern of this mixture showed a sharp (001) line corresponding to 10.66 Å, with an equally sharp (002) line at 5.34 Å. The absence of any hint of separation here indicates that the basal spacing probably is unchanged as Fe_2O_3 replaces Al_2O_3.

All the preparations just described also showed x-ray diffraction lines of α-C_4AH_{13} which, according to recent research [8,10], may contain CO_2. The relative amount of this phase increased as replicate x-ray runs were made on the same specimen. A weak line corresponding to the basal spacing of the monocarbonate ($3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$) also was noted, in a few cases, after further exposure. These observations are compatible with the explanation that the α-hydrate was formed progressively by the action of atmospheric CO_2 on the moist $C_4(A,F)H_{19}$ phase. It is of interest to note that these carbonated phases (possibly also containing Fe_2O_3 in substitution for Al_2O_3) form in the presence of liquid water, whereas the β-C_4AH_{13} type (see below) apparently is produced only on drying.

For a study of the hydrates of the β-C_4AH_{13} type, samples equivalent to those described above were filtered off and dried in a desiccator over saturated ammonium chloride solution (79% rh, approx.). X-ray diffraction patterns were made, following the usual procedure. As in the case of the fully hydrated materials, the patterns were dominated by the (001) and (002) reflections. An internal standard was introduced in order to make a closer measurement of the position of these lines. Small portions of the dried hydrates were ground with $Ca(OH)_2$, which furnishes a strong diffraction line between the (001) and (002) lines of the hydrates. For comparative purposes, the (002) line was chosen as affording better resolution than the (001). The appearance of the peaks, corrected as to position with reference to the standard, is shown in figure 1.
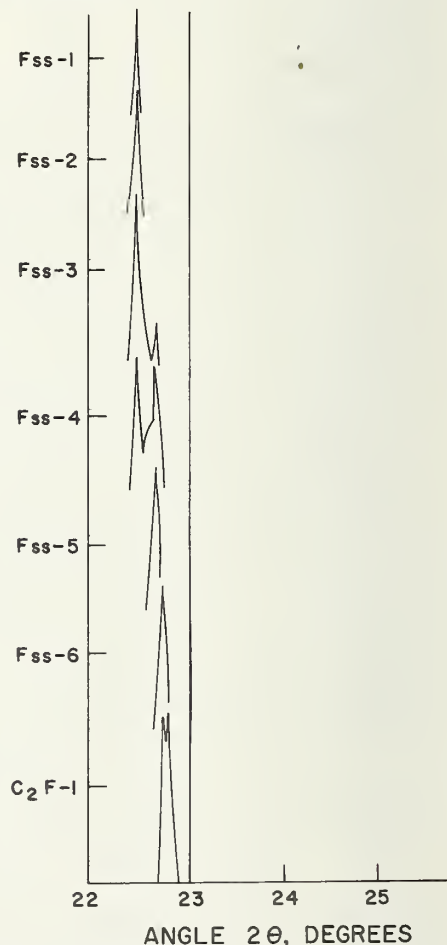

FIGURE 1. *Appearance of x-ray diffraction peaks corresponding to (002) reflection in series of* $C_4(A,F,)H_{13}$ *preparations.*

The outstanding feature here is the separation into a doublet in two of the intermediate members of the series. Reading downward, the peak at first appears constant in position. With the third member a second peak is observed, which becomes stronger in the fourth member. In the last three, only the latter peak occurs and the position appears to cha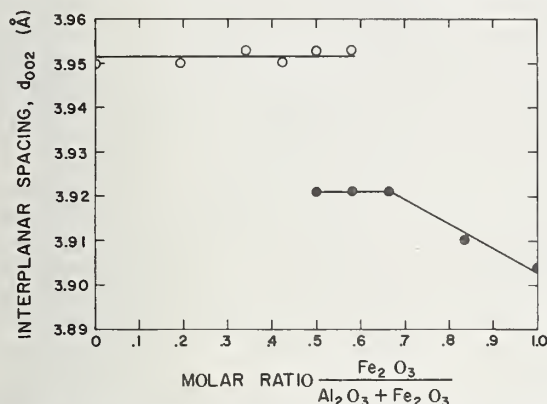nge slightly with composition. The relation between the position of these lines and composition may be seen more clearly in figure 2. The significance of the doublet is not clear. There may be two poly-types of the same composition, or it may be that the 19-hydrate which is formed initially breaks down on drying, forming two 13-hydrates differing in Fe_2O_3/Al_2O_3 ratio. No explanation is offered for the small doublet in the C_2F peak.

The d-spacings corresponding to the x-ray diffraction lines for this series are given in table 3, last 7 columns. Column 3 gives corresponding data for a preparation designed to contain half as much Fe_2O_3 as Fss–1 and hydrated by wet grinding with a mortar and pestle as described previously. Column 2 gives data for a sample of β–C_4AH_{13} prepared in an earlier investigation, while the first column gives, for reference, the corresponding spacings reported by Jones and Roberts [9]. Aside from the basal spacings discussed above, only two lines (not indexed) show a consistent trend, with varying composition, of sufficient magnitude to appear significant. Figure 3 is a plot of the spacings for these lines as functions of the composition. They start at 2.87 and 2.37 Å, respectively, for C_4AH_{13}, and increase with increasing Fe_2O_{13} content. The second of these lines is of low intensity.

FIGURE 2. *Interplanar spacing,* d_{002}, *of* $C_4(A,F)H_{13}$ *preparations in relation to composition; calculated from peaks shown in figure 1.*

TABLE 3. *Interplanar spacings for a series of calcium aluminoferrite hydrates of the* β-C_4AH_{13} *type, computed from x-ray powder diffraction patterns*

β-C_4AH_{13}[a]	β-C_4AH_{13}	$C_4(A,F)H_{13}$ series; $\frac{F}{A+F}$ =							C_4FH_{13}
		0.194	0.341	0.427	0.500	0.580	0.666	0.837	
7.9	8.0	8.05	7.96	7.98	7.88	7.88	7.84	7.81	7.80
4.95			4.90	4.95	4.92	4.87			
4.54	4.39	4.467	4.52						
3.95	3.96	3.95	3.953	3.950	3.953	3.953			
		3.80				3.921	3.921	3.910	3.904
3.62	3.62	3.62	3.639	3.642	3.63	3.642		3.64	
3.31						3.292		3.393	
2.88	2.873	2.870	2.902	2.899	2.902	2.908	2.919	2.919	2.936
2.86			2.871	2.870	2.871	2.868			
2.83			2.827	2.820	2.818		2.839	2.758	2.771
2.69	2.687	2.687	2.715	2.685	2.714	2.712		2.725	
2.63	2.638		2.638	2.636	2.630	2.621	2.620	2.628	2.627
2.49	2.512		2.512	2.510	2.521	2.518	2.520	2.514	2.517
2.47	2.475	2.474	2.479	2.478	2.482	2.491	2.485	2.489	
2.45	2.448		2.458	2.457	2.452	2.453	2.453	2.464	2.448
2.38	2.366	2.379	2.395	2.402	2.406	2.405	2.415		
2.31	2.304		2.304	2.317	2.326	2.321	2.325	2.312	2.263
2.24	2.235	2.233	2.244	2.242	2.248	2.249	2.254	2.254	2.246
2.21	2.206		2.216	2.211	2.202	2.198	2.194		2.216
2.17	2.174		2.173	2.177	2.163	2.166		2.166	2.176
2.05	2.055		2.054	2.057	2.053	2.055	2.052	2.051	2.063
1.98	1.979	1.987	1.977	1.980	1.992	1.988	1.983	1.975	1.981
1.94			1.941	1.958	1.955		1.970	1.955	
1.92	1.927			1.929	1.933	1.939		1.926	1.926
1.86			1.870	1.876	1.873	1.875			1.852
1.81	1.816		1.818	1.818	1.818	1.818			
1.80			1.790	1.798	1.796				
1.75	1.757					1.751			
	1.735								
	1.691		1.686	1.687	1.690	1.687			
			1.674	1.675	1.673	1.675			
	1.660		1.661	1.664	1.658	1.657			
1.66									
1.65									
1.64									
1.57	1.584		1.582	1.589	1.579	1.587			
1.55					1.563				

[a] From Taylor [2].
[d spacing in Å]

5
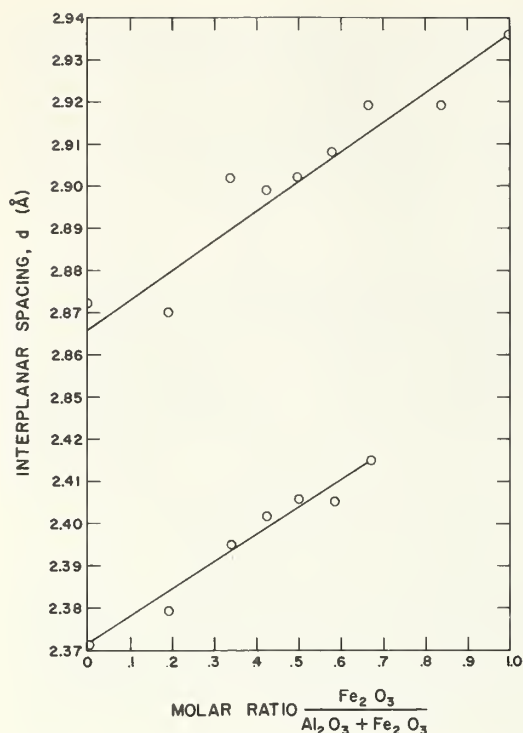
FIGURE 3. *Variation in* d-*spacings for two x-ray diffraction lines with composition of* $C_4(A,F)H_{13}$ *preparations.*

b. Isometric Series (Hydrogarnets)

X-ray diffraction patterns of the isometric series were obtained on preparations hydrated at temperatures slightly above room temperature (method C—see sec. 2). Samples were filtered off and dried over saturated NH_4Cl solution under reduced pressure. The typical hydrogarnet pattern was observed in all cases except with the hydrated C_2F preparation, which exhibited only the hexagonal pattern. Lines due to $Ca(OH)_2$ were also present and served as a standard for correction of the observed diffraction angles. The size of the cubic unit cell was determined from the calculated d-spacings.

Figure 4 shows the unit cell edge as a function of composition. In this plot, the open circles represent a series hydrated by wet grinding with mortar and pestle. The point at the $F/A+F$ ratio near 0.2 represents a mixture of C_3A and Fss–1 ground and hydrated together, while the others are for the regular series (table 1). During each hydration experiment the temperature rose from about 25 °C to 35–40 °C because of the heat developed by the motor and the insulating effect of the plastic tent. At this temperature the hydration product was a mixture of the isometric and hexagonal phases (with $Ca(OH)_2$), the former being strongly predominant in the high-Al_2O_3 end of the series. The three closed circles in figure 4 represent part of an earlier series hydrated in the same way, but sub-

sequently kept at 45 °C several days to insure complete conversion to the isometric hydrate. The rest of this earlier series was discarded because of evidence of separation of Fe_2O_3.

The two triangles were derived from another series hydrated by shaking with plastic beads in plastic bottles followed by several days of storage at 45 °C (method B). Here again, the rest of the samples in the series turned red and were discarded. The plotted point for C_3AH_6, at 12.573 Å, was taken from a previous report [4]. It is apparent that there is an approximately linear relationship between unit cell size and composition extending from C_3AH_6 at least to a point where five-sixths of the Al_2O_3 has been replaced by Fe_2O_3.

X-ray patterns of several other preparations gave values for a_o that departed from this linear relationship by amounts greater than could be attributed to uncertainties of measurement. The preparations yielding the anomalous results had all gone through the transition, hexagonal ⇌ isometric, at least partially, one or more times. The extent of the departures from the line may be seen in figure 5, in which the straight line is copied from figure 4. The open circles and semi-circles in figure 5 represent a series prepared at 1 °C, converted to the isometric phase at 45°C, to the hexagonal again at 1 °C, and finally to the isometric at 35 °C. The filled circle and semicircles represent two products, prepared at room temperature, which contained both the hexagonal and the isometric phases. They were subsequently kept several weeks at 1 °C, and finally converted to the isometric form at 35 °C. The four points at the left (semicircles) represent two doublet x-ray pattern peaks; a separate value of a_o was calculated for each set.

In order to verify the assumption that these departures from the norm were related in some way to phase transitions, a sample of Fss–2 was hydrated by wet grinding with mortar and pestle, in the presence of a slight excess of lime, and then put through a schedule of cooling and warming. Portions were filtered off for x-ray diffraction analysis at appropriate times. The schedule and results are given in table 4, and the calculated values of a_o are shown in figure 5 (triangles).

It is evident that the unit cell of the hydrogarnet phase increases slightly in size with changes in temperature across the transition zone between the hydrogarnet and hexagonal phases. Also, although in this case the evidence is scant, the change seems to occur when the temperature is lowered, and conversion to the hexagonal phase is favored. Assuming that the change in dimensions results solely from a change in composition, it is apparent that the hydrogarnet phase becomes richer in Fe_2O_3 during the temperature cycling. As a consequence, it must be inferred that part of the Al_2O_3 is liberated. It is assumed to be present as amorphous hydrated alumina, since there is, in some cases, no other observable crystalline phase to account for it.
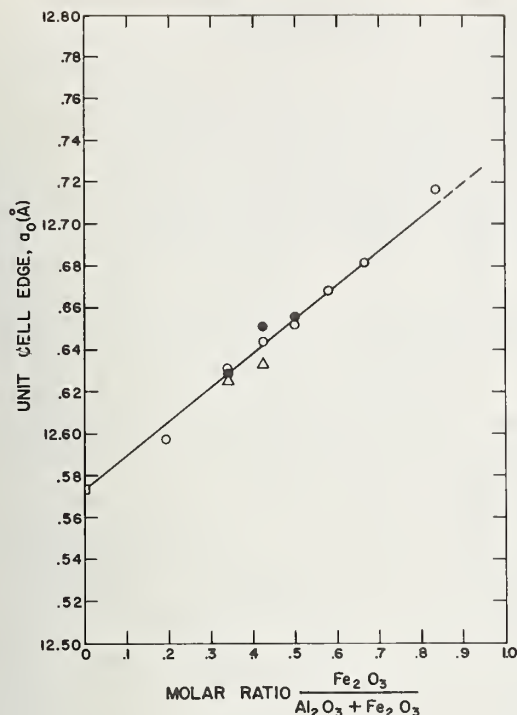
6

FIGURE 4. *Variation of unit cell edge with composition of $C_3(A,F)H_6$ preparations.*

Open circles: products prepared by method C (see sec. 2). Closed circles: same, with subsequent storage at 45 °C. Triangles: products prepared by method B. Square: from previous work [4].
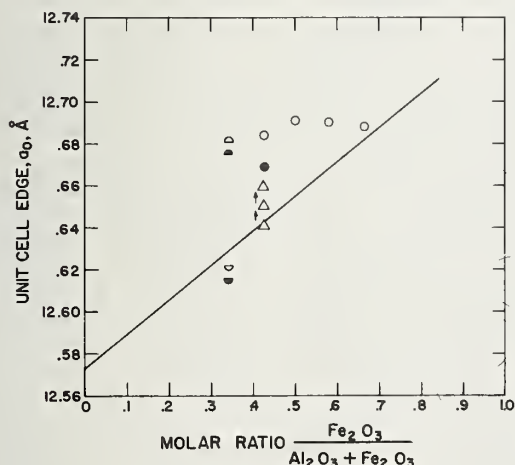

FIGURE 5. *Anomalous values of unit cell edge of $C_3(A,F)H_6$ preparations that had been converted to $C_4(A,F)H_n$ and back to $C_3(A,F)H_6$.*

Open circles and semicircles: products prepared at 1 °C, subsequently held at 45 °C, then at 1 °C, then at 35 °C. Closed circle and semicircles: prepared at room temperature, subsequently held at 1 °C, then at 35 °C. Semicircles indicate 2 distinct hydrogarnet phases in same preparation as shown by doublet peaks. Triangles: single preparation put through successive cycles of cooling and warming.

TABLE 4. *Effect of cycles of cooling and warming on the unit cell edge length (a_0) of a hydrogarnet preparation*

Treatment and temperature	Phases present[a]	Calculated a_0 in hg phase Å
Ground wet, $2\frac{1}{2}$ hr at about 30 °C	hg; $Ca(OH)_2$; very little hex	12.641
6 days at 15 °C	hg; $Ca(OH)_2$; increase in hex	12.653
2 days at 36 °C	hg; $Ca(OH)_2$; very little hex	12.651
20 days at 1 °C	mostly hex; hg; $Ca(OH)_2$	12.661
1 day at 38 °C	hg; $Ca(OH)_2$; very little hex	12.659

[a] hg = hydrogarnet.
hex = hexagonal plate phase.

3.4. Thermal Dissociation

The dissociation of the hydrates on heating was studied by means of differential thermal analysis with the apparatus described above and by determination of weight loss on heating at progressively higher temperatures in a covered crucible in an oven. Two series of samples were used for the DTA study, the first having been made by method C (see sec. 2) while the other consisted of the same group after storage at 1 °C to convert the isometric to the hexagonal hydrates. The samples had been filtered off and dried over NH_4Cl under reduced pressure. X-ray patterns showed the presence of minor amounts of the isometric phase in the preparations predominantly hexagonal; also the converse. These were, in most cases, detected by the DTA, so that in a general way all the patterns were similar. There were, of course, differences in relative intensities of the heat effects, as well as slight shifts in the temperatures at which these effects were observed.

Typical traces for the predominantly hexagonal series are shown in figure 6. The bottom trace in
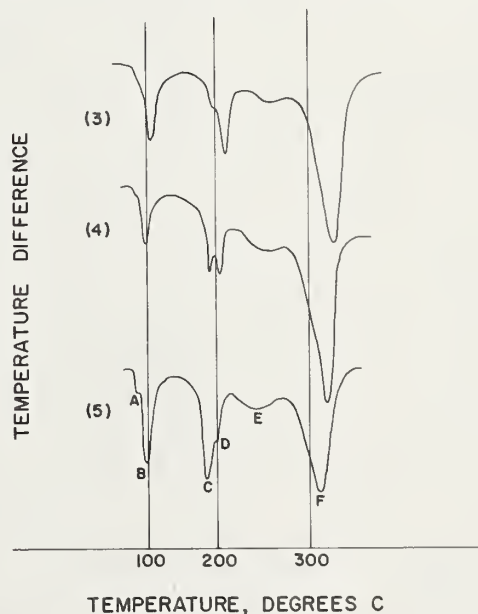

FIGURE 6. *DTA traces of three calcium aluminoferrite hydrate preparations.*

Figures in parentheses relate to experiment numbers in table 5.

this group shows six separate endothermal effects (labeled A through F). The first five of these appear to be associated with the hexagonal phase, or phases, since they were either absent or greatly reduced in magnitude in traces for the samples that were predominantly in the isometric form. The last endotherm, F, was strong in the traces of both the isometric and the hexagonal hydrates, with the exception of that of the hydrated C_2F in which it was entirely lacking.

Temperatures corresponding to these endotherms are given in table 5. In many cases the

TABLE 5. *Temperatures of endotherms on DTA traces for hydrates of the calcium aluminoferrite series*

No.	$\dfrac{Fe_2O_3}{Al_2O_3+Fe_2O_3}$	A	B	C	D	E	F
		°C	°C	°C	°C	°C	°C
1	0	(a)	127	(a)	194	(a)	323
2	0.194	(a)	(b)	(b)	200	(b)	310
3	.341	(a)	105	191	208	265	311
4	.427	(b)	97	186	203	264	304
5	.500	80	95	187	200	244	308
6	.580	(a)	100	187	200	254	305
7	.666	(a)	93	183	(a)	242	299
8	.837	(a)	(b)	183	(a)	240	290
9	1.000	(a)	110	180	(a)	240	(a)

a No endotherm observed.
b Endotherm present but too slight for measurement.

figures given are averages of two or more readings, since the data for the hexagonal and isometric series were treated as a single group for this purpose and a few duplicate runs were made.

Weight-loss determinations were made only on the hexagonal hydrate series. The samples used had been prepared by method A. The weight-loss method was not sufficiently sensitive to permit close correlation with the DTA results, but the results were of some assistance in deducing the significance of the various endotherms. Referring again to figure 6, the numbers in parentheses correspond to the same numbers in table 5. The first endotherm, A, was observed only in traces 4 and 5, and was too small to permit even a guess as to its origin. Endotherm B seems to be associated with the loss of 2 or 3 molecules of water and was detected in the DTA traces of all the hexagonal-phase samples. There is a trend toward lower temperatures as the Fe_2O_3 content increases, but there are also some irregularities (Nos. 6 and 9). Endotherms C and D appear to be closely related. The former is absent from the trace of the hydrate containing no Fe_2O_3, while the latter is not exhibited by the hydrates high in Fe_2O_3. Intermediate samples show a progressive change in the relative magnitudes, as may be seen in figure 6. It is possible that this double endotherm, as well as the double x-ray diffraction peak discussed earlier, is an indication of the presence of two phases differing slightly in composition or structure. The temperature of C drops slightly but fairly consistently with increasing Fe_2O_3 content, while that of D appears to go through a maximum.

Endotherm E was merely a shallow depression, insufficient to warrant any conjecture as to its

significance. The weight-loss determinations failed to separate these heat effects.

Endotherm F represents the first dehydration step of the isometric phase, $C_3(A,F)H_6$. Preparation 1, table 5, was made for this experiment by hydrating C_3A by the same procedure used with the aluminoferrite series. It was mainly C_3AH_6, but contained a little of the hexagonal phase. For this sample the temperature of endotherm F was 323 °C. A sample of C_3AH_6 prepared hydrothermally showed a similar break at 300 °C. With increasing Fe_2O_3 content, the temperature was progressively lower, reaching 290 °C for preparation 8. No. 9, containing no Al_2O_3, gave no indication of an endotherm in this region. It is inferred that no hydrogarnet phase was present in this sample. Slight irregularities in the composition-temperature relation probably result from slight differences in rate of heating.

Endotherm F was the major heat effect in all samples (except No. 9), whether the material was essentially in the isometric or the hexagonal form, with no observable difference in temperature between the two types. This fact could be explained either by a very close coincidence of dissociation temperatures for the two phases, or by a transformation of the hexagonal phase to the isometric during the course of the DTA. To check the latter possibility, a sample of calcium aluminate hydrate, initially about 90 percent C_4AH_{13} and 10 percent C_3AH_6, was heated to 250 °C over a period of 15 min in a covered crucible, roughly simulating the conditions present during the DTA run. An x-ray diffraction pattern subsequent to this treatment showed essentially complete conversion to C_3AH_6 and $Ca(OH)_2$. Samples of several of the aluminoferrite hydrates were heated in the same manner, with similar results.

From the foregoing experiments it is evident that in the DTA experiments with the hexagonal hydrates, endotherm F is preceded by a transformation to the isometric phase. This conclusion appears to be at variance with the results of other investigators [10,11,12,13] who have studied the thermal dissociation of C_4AH_{13}. However, it should be noted that the experimental conditions were quite different. In the present work the heating was of only a few minutes duration, and the water vapor pressure surrounding the crystals must have been close to 1 atm. In the dehydration experiments of Buttler et al. [11], the pressure of the water vapor was held at 6 mm.

Investigators who have studied the changes taking place in C_4AH_{13} on heating are not in complete agreement as to the reactions that occur. However, the existence of two lower hydrates, C_4AH_{11} and C_4AH_7, is widely accepted and amply supported by x-ray diffraction data. On this basis, it appears reasonable to associate the endotherms near 100 °C (A and B) with dehydration to the 11-hydrate and those near 200 °C (C and D) with the loss of 4 additional molecules of H_2O. It may be noted that the loss should be the same whether the product at this point is $C_4(A,F)H_7$

or $C_3(A,F)H_6 + Ca(OH)_2$. However, the x-ray patterns clearly indicate that the latter is the actual condition.

The weight-loss data obtained were compatible with the assumption of the loss of two molecules of H_2O at 100 °C and four additional molecules at 200 °C. The agreement was not quantitative, probably because of overlapping of reactions, among other factors. Approximately 2 molecules of H_2O remained after heating to 320 °C and most of this was lost at 550 °C.

3.5. Reactions of the Hydration Products With Calcium Sulfate Solutions

It is generally recognized that portland cements of relatively high alumina content are more susceptible to damage by sulfate waters than are cements low in alumina. It has been suggested that this difference in behavior may be due at least in part to differences in the nature or rate of reaction dependent upon the Fe_2O_3/Al_2O_3 ratio in the aluminoferrite phase and in its hydration products. It was therefore of interest to study the reaction between calcium sulfate and some of the hydration products obtained in the present work.

After some preliminary tests to ascertain the approximate rate of reaction, an experiment was set up to compare the reactions of the various hydration products by measuring the reduction in concentration of a calcium sulfate solution after a fixed period of reaction. The hydrated materials were the same as those used in the thermal dissociation study described above. They had been dried over saturated NH_4Cl solution under reduced pressure. There were two series, one in which the hydrate was nearly all of the hexagonal type, the other nearly all isometric. A weighed sample (0.14 g for the isometric series, 0.20 for the hexagonal) was placed in a small plastic bottle with 100 ml of an aqueous solution saturated with $CaSO_4$ and $Ca(OH)_2$. The tightly closed bottles were stored at room temperature (25–28 °C) for 29 days, after which time the solutions were analyzed for SO_3. Analyses of companion samples of the starting materials gave the quantities of Al_2O_3 and Fe_2O_3 present in the solids (the amounts in solution being negligible) and the amount of SO_3 taken up could therefore be computed in relation to the sesquioxides. A molar ratio of $3SO_3$ to $1(Al_2O_3, Fe_2O_3)$ would be required for complete conversion to a product of the ettringite type, while a 1:1 ratio would suffice for the monosulfate type, irrespective of the crystal species and stoichiometry of the starting material. Reactions leading to a product of the ettringite type may be formulated as follows:
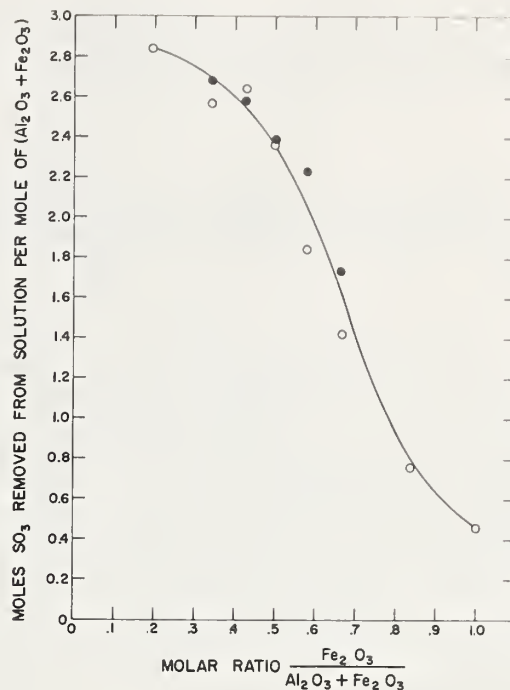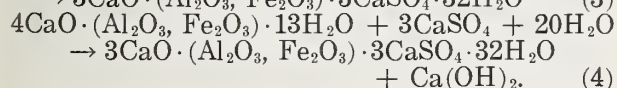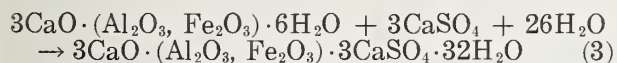
$$3CaO \cdot (Al_2O_3, Fe_2O_3) \cdot 6H_2O + 3CaSO_4 + 26H_2O$$
$$\rightarrow 3CaO \cdot (Al_2O_3, Fe_2O_3) \cdot 3CaSO_4 \cdot 32H_2O \quad (3)$$
$$4CaO \cdot (Al_2O_3, Fe_2O_3) \cdot 13H_2O + 3CaSO_4 + 20H_2O$$
$$\rightarrow 3CaO \cdot (Al_2O_3, Fe_2O_3) \cdot 3CaSO_4 \cdot 32H_2O$$
$$+ Ca(OH)_2. \quad (4)$$

FIGURE 7. *Removal of SO_3 from solution by calcium aluminoferrite hydrate preparations during storage for 29 days.* Open circles: hexagonal hydrates. Closed circles: isometric hydrates.

The results are shown in figure 7. The decrease in the amount of SO_3 in solution, converted to moles and divided by the number of moles of Al_2O_3 plus Fe_2O_3 present, is plotted as the ordinate. The abscissa expresses composition as in previous graphs.

The results have no quantitative significance aside from the particular samples used and the conditions of the experiment. Nothing is known as to surface area, an important factor in determining reaction rates. However, the hydrates were prepared in the same manner, and particle size probably was fairly uniform within a given series. No difference in size was apparent under the microscope. In comparing the hexagonal with the isometric series, however, it is impossible to estimate the relative surface areas, since the isometric crystals are nearly spherical, while the hexagonal exist as very thin plates. Hence the fact that the points for the two series fall close to a single curve (fig. 7) may be fortuitous. It is clear, nevertheless, that the relative reactivity toward $CaSO_4$ in solution decreases with increasing Fe_2O_3 content in the hydrates.

Microscopic examination of the residues showed almost complete conversion to needles, usually in spherulites, having the appearance of ettringite, for all samples high in Al_2O_3. Decreasing amounts were found as the Al_2O_3 content decreased and none at all in the last which contained no Al_2O_3. These observations were confirmed by x-ray dif-

9

fraction. The lines due to a phase of the ettringite type were predominant except near the high-Fe_2O_3 end of the series. Other lines, corresponding to calcium aluminate monosulfate hydrate, were found to increase in intensity toward the Fe_2O_3 end. Apparently the monosulfate phase formed first, as no needles were observed within the first 5 days in the preliminary tests.

4. General Discussion

During the past few years there has been a great deal of research on the tetracalcium aluminate hydrates [8,9,10,11,12,13]. As a result of the wealth of new data, the generally accepted ideas of the relationships of the different hydrates have been considerably altered. Although it would be premature to say that all the previous uncertainties have been cleared up, certain conclusions appear justified on the basis of the literature cited; (a) that the compound heretofore called β–C_4AH_{13}, having a basal spacing about 7.9 Å, is actually C_4AH_{12}; (b) that there is a compound previously designated α–C_4AH_{13} having a composition C_4AH_{13} and basal spacing about 8.2 Å; (c) that there is a derivative, containing half a mole or less of CO_2, having the same basal spacing of 8.2 Å.

The present work has not included any experimental study designed to fix the precise water content of the various hydration stages of the calcium aluminoferrites. It has been assumed, and confirmed at least approximately, that the water content is the same as that of the corresponding pure aluminates after similar treatment. The formula C_4AH_{13} has been familiar in the literature for several decades; hence it has been adhered to throughout the present paper, even though the works cited above make it appear highly probable that the β-form should be called C_4AH_{12}.

One objective of this study was to determine the relation between the Fe_2O_3/Al_2O_3 ratio of the hydrates and certain measurable properties or parameters that might serve as identifying characteristics, affording a means of estimating the composition of the respective hydrated aluminoferrites in a complex material such as hydrated portland cement. Numerous investigators have reported the occurrence of a phase of the C_4AH_{13} type in cement at certain stages of the hydration process, but there has been no way of ascertaining whether any Fe_2O_3 is present in solid solution. In the case of the isometric hydrate (C_3AH_6 type) there is still some doubt as to its presence in cement hydrated at ordinary temperatures, but it may exist in steam-cured cement.

From the data presented here, it is obvious that the substitution of Fe_2O_3 for Al_2O_3 in the calcium aluminate hydrates causes relatively slight changes in their measurable characteristics, especially over the range likely to be encountered in hydrated cements. In the case of the hexagonal (C_4AH_{13}) type of hydrate, the x-ray patterns show measurable shifts in certain lines, unfortunately not the strongest. Whether the splitting of the (002) peak near the middle of the range is a reliable and reproducible characteristic cannot be known without further study. The DTA traces also show slight shifts of peaks with changing composition, but these are even less useful than the x-ray patterns.

In the case of the isometric (C_3AH_6) series, the x-ray pattern provides a better index of composition, since there is a distinct increase in computed unit cell edge as the Fe_2O_3 content increases. The DTA results are of less value in this case as well, though the shift in dissociation temperature is somewhat greater than that for the hexagonal series. It should be borne in mind that the isometric hydrate, if it occurs in cement, is likely to contain silica in solid solution, resulting in further changes in unit cell size and probably in dissociation temperature.

Another useful index of composition in a solid solution series is the refractive index. During the course of this study, numerous attempts were made to obtain accurate measurements of the indices of refraction of both the hexagonal and the isometric series. Unfortunately the particles were very small (mostly of the order of 2 microns) and had a strong tendency to mat together on drying, so that the optical properties could not be determined with the precision necessary to be of use in estimating composition. From a practical standpoint, it is likely that conditions in a complex material like hydrated cement would be even less favorable.

Another objective was to ascertain the effect of substitution of Fe_2O_3 for Al_2O_3 on the reactions of the hydrates with calcium sulfate in solution. These reactions are of significance in connection with the normal setting and hardening processes of hydraulic cements and with the subsequent behavior of cements in the presence of sulfates in solution.

From the results of the work described in section 3.5, it appears that all the aluminoferrite hydrates reacted in the same manner, first forming the monosulfate, which subsequently was changed to the trisulfate (ettringite type) with an increase in the amount of SO_3 taken up. The rate of the reaction, however, decreased as the proportion of Fe_2O_3 increased. From these observations it is inferred that the superior resistance to sulfates exhibited by cements of high Fe_2O_3/Al_2O_3 ratio is not the result of a difference in the type of reaction product, but may be related to the rate of reaction with sulfate solutions.

No detailed study was made of the x-ray patterns of the sulfated products, so it cannot be stated with certainty that the Fe_2O_3/Al_2O_3 ratio remained the same as that in the unsulfated hydrates. However, there was no change in color of the solid residue; hence it may be inferred that no Fe_2O_3 was liberated during the reaction.

Certain results obtained in this study are of interest in relation to one of the more theoretical aspects of the problem, namely, the question of the composition of α-C_4AH_{13}. The view advanced by Seligmann and Greening [8] among others, that this phase is really a "semicarbonate", has been widely accepted. Alègre [12] and Lavanant [13], however, obtained α-C_4AH_{13} by careful dehydration of C_4AH_{19} with rigid exclusion of CO_2, and consider it to be the only 13-hydrate. Still more recently Dosch and zur Strassen [10] have concluded that there is an α-C_4AH_{13} and also a "quarter carbonate", the two having the same basal spacing of 8.2 Å.

In the present work, the fact that the 8.2 Å line appeared and grew in intensity during the course of repeated x-ray diffraction runs on samples of moist $C_4(A,F)H_{19}$ is evidence that CO_2 facilitates formation of the compound represented by the 8.2 Å spacing.

5. Summary

Calcium aluminoferrite hydrates in two series, $C_4(A,F)H_n$ (hexagonal plates) and $C_3(A,F)H_6$ (isometric), were prepared by hydrating the corresponding anhydrous aluminoferrites in various ways. Hydration of the end member, C_2F, yielded only the hexagonal type.

With all the aluminoferrite hydrates in contact with $Ca(OH)_2$ solution, a reversible reaction occurred between 15 and 35 °C, the hexagonal phase being stable below this temperature range and the isometric (hydrogarnet) phase above.

X-ray diffraction analysis of specimens of the hexagonal series, saturated with water, gave patterns like that of C_4AH_{19}. There was no detectable shift in the basal spacing with change in Fe_2O_3/Al_2O_3 ratio. Successive patterns obtained from the same mount showed gradual conversion to α-C_4AH_{13}, attributed to reaction with atmospheric CO_2.

When dried to the 13-hydrate stage (β-type) the hexagonal series gave x-ray patterns varying slightly with Fe_2O_3/Al_2O_3 ratio. The (002) reflection split into a doublet near the middle of the series, while two of the less prominent lines showed a consistent trend to larger d-spacings as the Fe_2O_3 was increased.

The x-ray patterns of the isometric series showed a linear relation between composition and unit cell edge, going from 12.573 for C_3AH_6 to 12.716 for the member having approximately $\frac{5}{6}$ of the Al_2O_3 replaced by Fe_2O_3.

Differential thermal analysis traces of the isometric series showed a large endothermic effect near 300 °C. The temperature ranged downward from 323 °C for C_3AH_6 to 290 °C for the number highest in Fe_2O_3. The hexagonal series gave more complicated patterns, with peaks of moderate size near 100 and 200 °C and a larger one near 300 °C. The first two varied only slightly in position with change in Fe_2O_3/Al_2O_3 ratio. The third proved to be identical with the peak exhibited by the isometric series and it was found that the hexagonal hydrate was converted to the isometric during the course of the DTA run.

All the aluminoferrite hydrates reacted with calcium sulfate solution forming mixtures of the monosulfate and trisulfate (ettringite) types, the latter predominating at later stages. The rate of reaction decreased as the Fe_2O_3/Al_2O_3 ratio of the hydrate increased.

6. References

[1] F. M. Lea and C. H. Desch, The Chemistry of Cement and Concrete, 2d ed., Edward Arnold, Ltd., London (1956). Ch. IV.

[2] The Chemistry of Cements, edited by H. F. W. Taylor, Academic Press, New York (1964). Vol. 1, Chapter 2, by J. H. Welch.

[3] A. J. Majumdar, The ferrite phase in cements, Trans. Brit. Ceram. Soc. 64, 105–119 (1965).

[4] E. T. Carlson, Action of water on calcium aluminoferrites, J. Res. NBS, 68A, 453–463 (1964).

[5] G. Malquori and V. Cirilli, The hydrated calcium ferrites, and the complexes that originate from tricalcium ferrite by association with different salts of calcium (Note 4), (in Italian), Ric. Sci. 14, 78–84 (1943).

[6] S. Chatterji and J. W. Jeffrey, Studies of early stages of paste hydration of cement compounds, I, J. Am. Ceram. Soc. 45, 536–543 (1962).

[7] H. E. Schwiete and T. Iwai, The behavior of the ferritic phase in cement during hydration, (in German) Zement-Kalk-Gips 17, 379–386 (1964).

[8] P. Seligmann and N. R. Greening, New techniques for temperature and humidity control in x-ray diffractometry, J. Res. and Devel. Labs., Portland Cement Assn. 4, (2), 2–9 (1962).

[9] F. E. Jones and M. H. Roberts, The system CaO-Al_2O_3-H_2O at 25 °C, Bldg. Research Current Papers, Research Series 1, Dept. of Sci. and Indus. Research, London (1962).

[10] W. Dosch and H. zur Strassen, Investigation of tetracalcium aluminate hydrate. I. The various hydrate stages and the effect of carbonic acid, (in German) Zement-Kalk-Gips 18, 233–237 (1965).

[11] F. G. Buttler, L. S. Dent Glasser, and H. F. W. Taylor, Studies on $4CaO \cdot Al_2O_3 \cdot 13H_2O$ and the related natural mineral hydrocalumite, J. Am. Ceram. Soc. 42, 121–126 (1959).

[12] R. Alègre, Investigations on the hexagonal hydrated tetracalcium aluminate, (in French) Rev. mater. construc. trav. publ. No. 566, 301–314 (1965).

[13] F. Lavanant, Contribution to the study of some calcium aluminate hydrates, (in French) Rev. mater. construc. trav. publ. No. 592, 1–10, No. 593, 76–87, No. 595, 193–207, No. 596, 251–261, No. 597, 298–304 (1965).

Announcement of New Publications in
Building Science Series

Superintendent of Documents,
Government Printing Office,
Washington, D.C., 20402

Dear Sir:

Please add my name to the announcement list of new publications to be issued in the series: National Bureau of Standards Building Science Series.

Name _____

Company _____

Address _____

City _____ State _____ Zip Code _____

(Notification key N–339)

THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. Its responsibilities include development and maintenance of the national standards of measurement, and the provisions of means for making measurements consistent with those standards; determination of physical constants and properties of materials; development of methods for testing materials, mechanisms, and structures, and making such tests as may be necessary, particularly for government agencies; cooperation in the establishment of standard practices for incorporation in codes and specifications; advisory service to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; assistance to industry, business, and consumers in the development and acceptance of commercial standards and simplified trade practice recommendations; administration of programs in cooperation with United States business groups and standards organizations for the development of international standards of practice; and maintenance of a clearinghouse for the collection and dissemination of scientific, technical, and engineering information. The scope of the Bureau's activities is suggested in the following listing of its three Institutes and their organizational units.

Institute for Basic Standards. Applied Mathematics. Electricity. Metrology. Mechanics. Heat. Atomic Physics. Physical Chemistry. Laboratory Astrophysics.* Radiation Physics. Radio Standards Laboratory:* Radio Standards Physics; Radio Standards Engineering. Office of Standard Reference Data.

Institute for Materials Research. Analytical Chemistry. Polymers. Metallurgy. Inorganic Materials. Reactor Radiations. Cryogenics.* Materials Evaluation Laboratory. Office of Standard Reference Materials.

Institute for Applied Technology. Building Research. Information Technology. Performance Test Development. Electronic Instrumentation. Textile and Apparel Technology Center. Technical Analysis. Office of Weights and Measures. Office of Engineering Standards. Office of Invention and Innovation. Office of Technical Resources. Clearinghouse for Federal Scientific and Technical Information.**

---

*Located at Boulder, Colorado, 80301.
**Located at 5285 Port Royal Road, Springfield, Virginia, 22171.